PRECOMBUSTION REMOVAL OF MERCURY FROM COAL BY MILD PYROLYSIS

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Keywords: mercury in coal, mild pyrolysis, clean coal

INTRODUCTION

Coal combustion is one of the most popular sources for energy in the United States. However, increasing environmental regulations concerning the emissions of various pollutants resulting from coal combustion are being promulgated. Title III of the 1990 Clean Air Act Amendments specifies that air toxics will be controlled to the maximum extent technically possible (maximum available control technology, MACT). A number of compounds listed as toxic are found in coal and are released into the atmosphere when coal is burned. Under Title III, a plant that emits over 10 tons/year of any one of the listed toxic compounds, or emits over 25 tons/year (or more) of any combination of these pollutants are required to comply to the control standards. Mercury is present in coal at varying ppm (μg/g) levels and is considered to pose a significant environmental health risk from coal combustion. Reviews[1] on mercury in the ambient air have suggested that the average concentration of mercury in the gaseous form in regionally polluted areas, such as the east coast, are in the range between 3 to 4 ng Hg/m^3. And in urban air the average concentrations may be as high as 10 ng Hg/m^3. Coal combustion has been estimated to account for over 8 % of the mercury emissions to the atmosphere.[2] Lindberg[3] reported that in the plume of a coal-fired power plant, gaseous mercury is present in excess of 1000 ng Hg/m^3 within a few kilometers of the source. Material balances on mercury in power plants have shown that only approximately 10% of the total mercury from the coal is found in the fly ash, and the remainder exits the stack in vapor form.[4, 5] Other studies investigating the effects of existing flue gas clean-up (FGC) technologies on mercury concentration in flue gases report that varying levels of removal can be achieved, ranging from 10% to 90% removal.[6, 7, 8, 9] This large variation is most likely due to differences in combustion reactors as well as differences in the chemical form of mercury and variations in chlorine levels in the feed coal.

The terminology of pyrolysis is used to refer to the processes in which coal is heated in the absence of oxygen. The coal partially decomposes and produces gaseous, liquid and solid residuals. Mild pyrolysis is performed using low temperatures (<600°C), low pressure (about 1 atm.) and usually low heating rates. The original coal matrix remains largely intact while the heating value of the coal is retained. Mild pyrolysis of coal has been shown to be an economically and technically viable method of desulfurization and denitrification.[10, 11] Most "organic" sulfur in Ohio #8 coal is released below 500°C in the form of H_2S which can be quickly scrubbed by solid sorbents. During pyrolysis the majority of trace elements in coal are retained in the solid residue, but volatile elements such as mercury, bromine, and antimony are released in vapor form. Elemental mercury has a low boiling point (356 °C) and has been shown to be released from coals at the lower temperatures indicative of mild pyrolysis.[12,13,14] The release of mercury from the coal structure before combustion by mild pyrolysis offers the greatest potential for the separation of mercury and its compounds from the evolved gases and vapors. The concentration of these species are at their greatest in the vapor phase during this period and may be collected by means of adsorption or chemisorption to solid sorbents. This precombustion removal represents a pollution prevention strategy. (Regulations controlling the release of mercury will most likely be promulgated in the future for coal burning power plants.)

This study investigates the influences of temperature and residence time on the evolution of mercury from coal during mild pyrolysis. While optimizing the temperature and residence time so as to maximize the evolution of mercury, it was also important to maintain the original heating value of the parent coal.

MILD PYROLYSIS METHODOLOGY

A Lower Freeport #6A coal mined in Harrison County, Ohio was the primary coal investigated in this study. The Lower Freeport sample was sieved to 115 x 150 mesh (~115μm) size prior to shipment. During the sieving and shipment time period the sample lost some moisture and became slightly oxidized. The condition of the sample as received was maintained by storing it with CO_2 headspace in poly-urethane containers. A Pittsburgh #8 Coal mined in Greene County, Pennsylvania was also used in this study so as to provide a comparison. This sample was also sieved to 115 x 150 mesh (~115μm) size and was maintained in an as received condition by storing it with CO_2 headspace in poly-urethane containers. The two parent coal samples examined in this study are high volatile bituminous coals. The original samples were riffled for characterization tests, and a summary of the test results is shown in Table 1.

The mild pyrolysis process was carried out in a Lindberg tube furnace with nitrogen flow. A diagram of this system is shown in Figure 1. It is a well known fact that trace values for mercury in coal vary largely even within a single coal seam. Before pyrolyzing the coal samples, it was necessary to extract a portion of the coal (~10grams), cone and separate that portion so as to produce a homogenized sample, and then determine a mean value for the mercury content of that homogenized sample. Samples to be pyrolyzed were then extracted from the homogenized sample, weighed to 0.5g ± 0.1mg, and placed in nickel alloy sample boats. The tube furnace was stabilized at a predetermined temperature, and the nitrogen flow was regulated so that the gas velocity in the hot zone of the tube was maintained at approximately 3cm/s.

Each sample was placed in the cool zone of the tube and purged of any trapped gases by the nitrogen flow. The sample was then pulled into the hot zone of the tube furnace and heated for a predetermined time. The sample was then pushed back into the cool zone of the tube where it remained in a nitrogen atmosphere until room temperature was achieved. The pyrolyzed coal was then analyzed for total mercury content using the ASTM D3684-78 procedure. The ASTM method was written specifically for fresh coal samples, but should effectively mineralize the pyrolyzed coal as well.

EXPERIMENTAL RESULTS AND DISCUSSION

Coal samples were subjected to mild pyrolysis conditions and percent removal of mercury was determined by comparing the final total mercury content of each pyrolyzed sample with an initial mercury value. The initial mercury value for each sample was calculated by multiplying the weight of the sample prior to pyrolysis with the mean mercury value which was established for the homogenized coal from which the sample was extracted.

The results are shown in Table 2, and graphical representations of the mercury removal as a function of temperature are shown in Figures 2 and 3. The data indicate a general trend within each residence time data set in which the percent removal increases with temperature rise, peaks at some temperature, and then declines. Thermomechanical analysis of both parent coals revealed that the two coals become fluid at about 400°C and remain fluid until resolidification occurs at 464°C for the Lower Freeport sample and 477°C for the Pittsburgh coal sample. When a coal is heated at temperatures in which it becomes plastic, a soft layer develops on the outside of the coal particles and internal depolymerization occurs. As the carbon becomes soft, it swells and traps gases. Once the coal becomes more plastic, the gases break through. It is possible that once the coal becomes plastic, the evolution of the mercury is greatly inhibited by this trapping action. The increased heating rate accompanying the higher temperatures increases the trapping because the devolatilization is greater than the plasticity.

Within each temperature range data set, a general trend exists in which the removal of mercury initially increases rapidly with residence time and then levels off as it seemingly approaches an asymptotic limit. This suggests that under the conditions given in the methodology, the rate of evolution of total mercury is proportional to the fraction of mercury and its compounds remaining in the char at any time multiplied by some reaction rate coefficient dependent on temperature. This can be expressed as a first order homogeneous decomposition with an asymptote dependent on temperature, time, reactor configuration, pressure, heating rate, and particle size:

$$\frac{X}{X_{max}} = 1 - e^{-kt}$$

Where: X = percent conversion
X_{max} = maximum percent available for conversion under a specified set of conditions
t = reaction time (min)
k = reaction rate coefficient (min^{-1})

By maximizing the regression coefficient when comparing the experimental data to the linear form of the equation, X_{max} can be obtained for each temperature. The slope of the linearization provides a value for k, the reaction rate coefficient. Table 3 lists the values of X_{max} with the corresponding R^2 and k for both coal samples and all temperatures. A comparison of the Lower Freeport #6A data with the above equation indicates a reasonable agreement between theory and measurements for all temperatures except 275°C and 325°C. The Lower Freeport #6A data indicates an interesting trend once a pyrolysis temperature of 325°C is achieved. Below this temperature, analysis results in a maximum possible removal of 100%, but after 325°C, X_{max} increases with temperature until it peaks at 500 °C. A comparison of the Pittsburgh #8 data with the equation, however, indicates a reasonable agreement between theory and measurements only within the temperature range of 325°C to 400°C.

By applying Arrehnius' law to the Lower Freeport #6A experimental data, a plot of ln(k) vs. 1/T results in figure 4. The plot shows two regimes for mercury removal in the Lower Freeport #6A coal. The data produces a straight line with a large slope in the 275°C to 400°C temperature range. This indicates a large activation energy, E, which can be associated with

chemical reaction control. The temperature at which the plot's slope changes dramatically, indicating a shift in controlling mechanism of the reaction, coincides with the coal's plastic zone. Application of Arrehnius' law to the Pittsburgh #8 experimental data results in figure 5. The plot indicates that the Pittsburgh #8 coal behaves similar to the Lower Freeport #6A coal under the pyrolysis conditions given in the methodology. The activation energies for the mercury removal in the lower temperature region (<400°C) are calculated using information from the equation of the straight line plotted in that temperature region. The activation energies for mercury removal from the Lower Freeport #6A coal and the Pittsburgh #8 coal are 6615 cal/gmol and 4939 cal/gmol respectively.

After treating a coal by mild pyrolysis, it is important to examine what effects the pyrolysis process has had on the overall heating value of the coal. An oxygen bomb calorimeter was used to determine the net heat of combustion of each of the Lower Freeport #6A pyrolyzed samples. These values were compared to an initial heat of combustion value which was calculated using the inital sample weight and a mean value for the net heat of combustion of the parent Lower Freeport #6A coal. Figure 6 shows a plot of this comparison. The results indicate that there is little change in the overall heating value of the Lower Freeport #6A pyrolyzed coal until pyrolysis temperatures are greater than 400°C. During the 200-400 °C temperature range, there is apparently little carbon loss although devolatilization of other components does occur. Once temperatures exceed 400 °C, there is a decrease in overall heating value which drops with temperature rise.

CONCLUSIONS

Given the conditions of the reactor used in this study, mild pyrolysis of coal can achieve up to 74% removal of mercury from the Lower Freeport #6A coal investigated and up to 80% removal of mercury from the Pittsburgh #8 coal investigated. The results show that precombustion removal of mercury from coal by mild pyrolysis can be modeled as a homogeneous reaction with a distinct maximum percent mercury available for conversion and a distinct reaction rate coefficient for each temperature range. The results also indicate that removal of mercury occurring when pyrolysis is performed at low temperatures (<400°C) on plastic or caking coals is characterized by chemical reaction control. At these low temperatures, the coal matrix suffers little destruction. The results verify that the overall heating value of the coal is essentially unaffected by mild pyrolysis at temperatures lower than 400 °C.

Table 1: Summary of Characterization Analysis on Original Coal Samples

	Lower Freeport #6A (Harrison Co., OH)		Pittsburgh #8 (Greene Co., PA)	
	As Determined	Dry Basis	As Determined	Dry Basis
%Ash	11.52	11.65	10.00	10.25
%Carbon	68.03	68.78	73.41	75.22
%Hydrogen	5.07	5.13	5.2	5.33
%Nitrogen	1.62	1.64	1.67	1.71
%Sulfur	4.24	4.29	1.09	1.12
%Oxygen (difference)	9.52	9.62	8.63	8.84
%Moisture	1.09 (residual)		2.40	
Density, g/cm^3		1.294		1.293
Hg Conc., ppm		0.57 ± 0.07		0.12 ± 0.04
Surface Area, m^2/g		1.105		1.386
Btu/lb	12,870	13,019	13,207	13,532
kJ/kg	29,933	30,280	30,717	31,473

Figure 1: Furnace with Nitrogen Flow

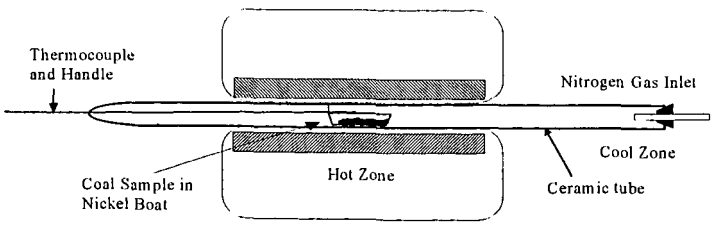


Table 2: Mild Pyrolysis Test Results

	Lower Freeport #6A %Removal of Mercury				Pittsburgh #8 %Removal of Mercury				
Temp. °C	2 Minute Residence Time	4 Minute Residence Time	8 Minute Residence Time	10 Minute Residence Time	2 Minute Residence Time	4 Minute Residence Time	6 Minute Residence Time	8 Minute Residence Time	10 Minute Residence Time
275	0	5.5	5.6	5.3	-	-	-	-	-
300	0	8.0	14.9	24.2	-	-	-	-	-
325	0	37.6	29.5	41.4	0	0	-	36.1	52.0
350	14.0	33.6	44.8	48.6	-	-	-	-	-
400	39.9	50.3	57.7	57.7	53.0	70.6	79.6	-	-
450	9.7	58.8	68.4	68.1	47.0	46.6	46.9	-	-
500	-	62.4	73.9	-	-	-	-	-	-
600	-	49.5	59.1	-	-	-	-	-	-

Figure 2: Lower Freeport #6A Mild Pyrolysis Data

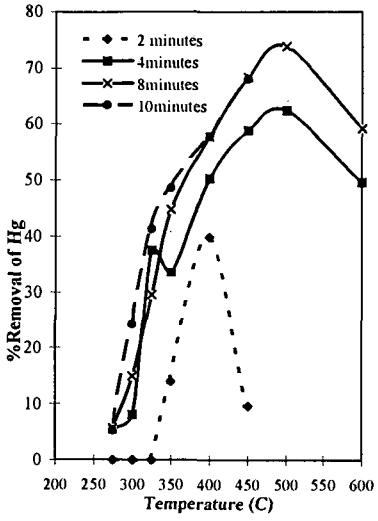


Figure 3: Pittsburgh #8 Mild Pyrolysis Data

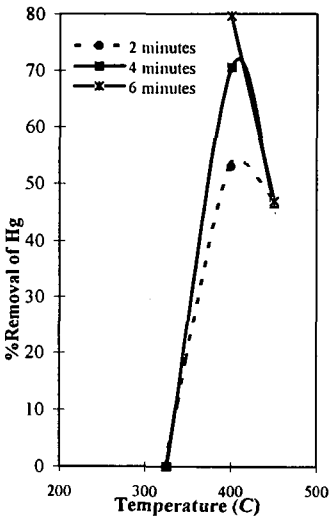


Table 3: Values of X_{max}, R^2, and k

	Lower Freeport #6A			Pittsburgh #8		
Temp.(°C)	X_{max}	R^2	$k(min^{-1})$	X_{max}	R^2	$k(min^{-1})$
275	1.00	0.683	0.006	-	-	-
300	1.00	0.939	0.028	-	-	-
325	1.00	0.657	0.044	1.00	0.850	0.071
350	0.54	0.993	0.234	-	-	-
400	0.58	0.972	0.502	0.86	0.998	0.441
450	0.70	0.931	0.449	1.00	0.598	0.097
500	0.77	0.999	0.422	-	-	-
600	0.62	0.999	0.386	-	-	-

Figure 4: Arrehnius Plot of Lower Freeport #6A Data

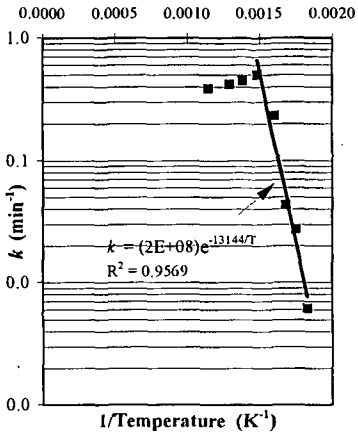


Figure 5: Arrehnius Plot of Pittsburgh #8 Data

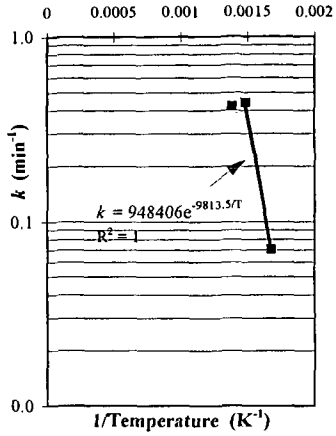
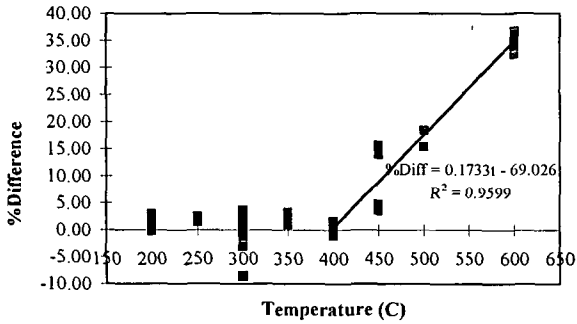


Figure 6: Comparison of Lower Freeport #6A Parent Coal and Pyrolyzed Coal Heating Values



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